

The University of Chicago

A STUDY OF ADDITION OF
HALOGEN ACIDS TO UNSATURATED
COMPOUNDS

A PART OF A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYSICAL
SCIENCES IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1931

By
MARY ADELINE BLOODGOOD

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INTRODUCTION

The ability of the ethylene derivative $R_1CH=CHR_2$ to exist in two electro-isomeric forms depends upon the electronegative character of the groups R_1 and R_2 . The comparative electronegativity of two radicals may be determined by splitting the organomercury compound, R_1HgR_2 , with hydrogen chloride, the more electronegative radical combining with hydrogen to form the corresponding hydrocarbon. From a series of such determinations a table of electronegativities has been compiled by Kharasch and Marker.¹

Kharasch and Darkis² have definitely isolated two forms of 2-pentene and this work has been repeated and confirmed by various other workers.³ In a molecule of this type, however, there is always a possibility of cis-trans isomerism. The separation of cis and trans isomers of the liquid pentenes or of any other unsaturated compound is extremely difficult.⁴ Therefore, in choosing a compound for this study it was desirable to select one whose cis and trans isomers differed in physical properties.

In order to exist in electromeric forms, an ethylene derivative must be composed of two radicals which are very nearly

¹Kharasch and Marker, J.A.C.S., **48**, 3130 (1926).

²Kharasch and Darkis, Chem. Reviews, **5**, 571 (1928).

³Sherrill, Otto and Pickett, J.A.C.S., **51**, 3023 (1929).
Sherrill, Baldwin and Hass, J.A.C.S., **51**, 3034 (1929). Clark and Hallonquist, Trans. Roy. Can., (3) **24**, Sect. 3, 115 (1930).

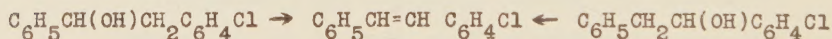
⁴Van de Walle (Bull. soc. chim. Belg., **27**, 209 [1913]) found it impossible to separate the cis-trans isomers of bromoethylene by distillation, freezing or solution in different solvents. He finally separated the two isomers by fractionation of azeotropic mixtures with absolute alcohol.

alike in electronegative character. According to Kharasch and Flenner,⁵ p-chlorophenyl is almost equal in electronegativity to the phenyl radical, and, therefore, these two radicals as they exist in p-chlorostilbene were chosen for this work. However, from the present method of analysis, it is impossible to predict the exact difference in electronegativity and just what interplay of forces would be exhibited in the molecule and whether it would be an ideal case for the study of electro-isomerism. The more recent work of Kharasch and Pines⁶ indicates that a better choice of radicals would have been p-chlorophenyl and o-chlorophenyl or o-chlorophenyl and m-chlorophenyl, as radicals within the triad are closer in electronegative character.

OUTLINE OF PROBLEM

The object of this work was threefold, namely: to attempt to prepare the electromers of p-chlorostilbene, to study the addition of unsymmetrical reagents to p-chlorostilbene, and to compare the addition reactions of cis and trans p-chlorostilbene.

The method selected to prepare p-chlorostilbene was dehydration of the corresponding alcohols: phenyl-p-chlorobenzylcarbinol and p-chlorophenyl-benzylcarbinol.



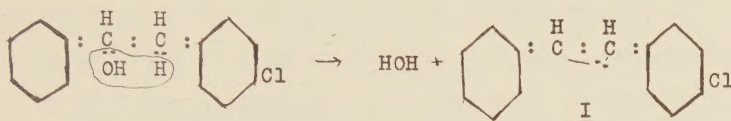
By means of these reactions it should be possible to prepare electromers of p-chlorostilbene unless one electromer is much more stable than the other.

In phenyl-p-chlorobenzylcarbinol, the removal of water

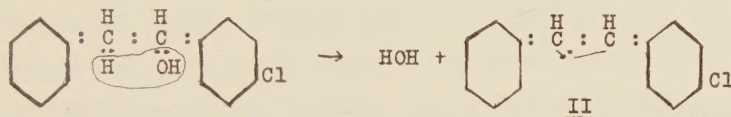
⁵Kharasch and Flenner, University of Maryland Publication.

⁶Kharasch and Pines, unpublished work.

would leave the second pair of electrons in the double bond closer to the carbon adjacent to the p-chlorophenyl radical.



With p-chlorophenyl-benzyl-carbinol, water is removed in the following manner:



This results in a form of p-chlorostilbene which is electronically different from that derived from phenyl-p-chlorobenzyl-carbinol. These two forms of p-chlorostilbene should have different chemical and physical properties. The melting points of the two should be slightly different and the addition of one should lower the melting point of the other. The two forms of p-chlorostilbene should add unsymmetrical reagents to form different compounds. For example, I should add hydrogen iodide to give phenyl-p-chlorobenzyl-methyl-iodide, while II should give p-chlorophenyl-benzyl-methyl-iodide.

The third phase of this problem was to prepare cis p-chlorostilbene and to compare its addition reactions with those of trans p-chlorostilbene. It has been suggested that the difference in the addition of hydrogen bromide to the 2-pentenes might be due to the existence of cis-trans isomers rather than electrical isomers and it was desirable to ascertain if geometric isomers could be distinguished by their addition reactions.

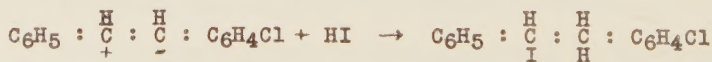
SUMMARY OF RESULTS

Although it was impossible to obtain p-chlorostilbene in

electromeric form, a number of very interesting facts were obtained from this investigation.

In the preparation of phenyl-p-chlorobenzyl-carbinol, the intermediate magnesium addition product of the Grignard reaction was isolated from the ether solution in the form of a stable etherate. Under appropriate conditions, the molecule of ether with which the addition product was combined, could be removed and the resulting ether-free substance would readily absorb ether, forming again the original etherate. The corresponding addition product in the preparation of p-chlorophenyl-benzyl-carbinol, although too soluble to be obtained from the reaction mixture, was precipitated from the ether solution by the addition of petroleum ether. These compounds are stable for a long period of time if properly protected from moisture. Even when exposed to air, they take up atmospheric moisture only very slowly.

As far as could be determined, p-chlorostilbene derived from phenyl-p-chlorobenzyl-carbinol gave a hydrogen iodide addition product which was identical to that obtained from the unsaturated derivative of p-chlorophenyl-benzyl-carbinol. In both cases the addition product consisted of a mixture of phenyl-p-chlorobenzyl-methyl-iodide and p-chlorophenyl-benzyl-methyl-iodide in the approximate ratio of 75% of the former to 25% of the latter. The stable form of p-chlorostilbene would be that in which the more electronegative phenyl radical repels the doublet to the carbon atom adjacent to the p-chlorophenyl radical, making the carbon atom relatively negative, and directing the addition of hydrogen iodide in the following manner:



This mechanism accounts for the larger amount of phenyl-p-chlorobenzyl-methyl-iodide formed in the addition of hydrogen iodide to p-chlorostilbene. This reaction illustrates the importance of the electronegative series in predicting the course of a reaction.

Both phenyl-p-chlorobenzyl-methyl-iodide and p-chlorophenyl-benzyl-methyl-iodide are reduced by an excess of hydrogen iodide to symmetrical phenyl-p-chlorophenyl-ethane identical to the substance formed by hydrogenation of p-chlorostilbene in the presence of palladium catalyst.

Cis p-chlorostilbene was prepared by half-reduction of p-chlorotolane. From a study of its reactions, it can be definitely stated that geometric isomers, unlike electromers, give the same addition products with unsymmetrical reagents, although the rate of addition is much more rapid for the cis than for the trans form. Similarly, cis and trans p-chlorostilbene gave the same hydrogenation product when the reduction was carried out in the presence of palladium.

DISCUSSION

p-Chlorostilbene was first prepared by Walther and Wetzlich⁷ by the condensation of benzaldehyde and p-chlorophenyl acetic acid when heated for twenty hours in a sealed tube at 300°. Later, Walther and Raetze⁸ prepared it by heating p-chlorobenzaldehyde and phenyl acetic acid in a tube at 250° for eight hours.

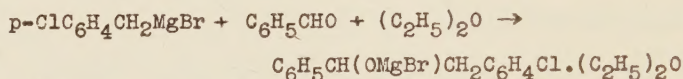
As high temperature and pressure may affect the electronic structure of a molecule, the p-chlorostilbene in this study was prepared by the dehydration of phenyl-p-chlorobenzyl-carbinol and

⁷Walther and Wetzlich, J. Pr., 61, 195 (1900).

⁸Walther and Raetze, J. Pr., 65, 283 (1902).

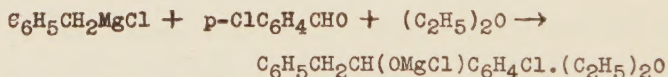
p-chlorophenyl-benzyl-carbinol.⁹

Phenyl-p-chlorobenzyl-carbinol was prepared by the Grignard reaction and, by controlling the condition of the experiment, it was possible to isolate the intermediate magnesium addition product in the form of an etherate.



By heating the etherate in vacuum, the molecule of ether was removed quantitatively with the formation of the free intermediate Grignard addition product, which, however, is the less stable modification as it readily absorbs ether to form the etherate. The isolation of the intermediate product made it possible to obtain the alcohol in a pure form while if the intermediate product was not isolated, the hydrolyzed product came out in the form of a yellow oil which crystallized slowly and incompletely upon long standing.

In the preparation of p-chlorophenyl-benzyl-carbinol, a solid intermediate product could be obtained only upon addition of petroleum ether. The greater solubility in ether of this intermediate product may be due to the use of the chloride to prepare the Grignard reagent.



p-Chlorophenyl-benzyl-carbinol yielded an unsaturated derivative which was identical to that from phenyl-p-chlorobenzyl-carbinol on the basis of melting points of mixtures of the two.

It was originally planned to study the hydrogen bromide addition compounds of p-chlorostilbene following the same proced-

⁹Ramart and Amagat (*Ann. Chim.*, (8) 10, 314 [1927]) have prepared p-methyl-stilbene by the dehydration of p-methyl-phenyl-benzyl-carbinol.

ure that was used with the 2-penten-1,2. However, as the bromides were a very low melting solid and an oil which gave no index of refraction, the hydrogen iodide addition products were chosen after preliminary examination showed them to be well defined crystalline substances.

The most satisfactory conversion of phenyl-p-chlorobenzyl-carbinol and p-chlorophenyl-benzyl-carbinol into the corresponding iodides was accomplished in a glacial acetic acid solution of hydrogen iodide.

The addition of hydrogen iodide to the unsaturated derivative of phenyl-p-chlorobenzyl-carbinol and p-chlorophenyl-benzyl-carbinol was carried out in glacial acetic acid,¹⁰ benzene and n-heptane, all reactions taking place in the dark. After two days, the normal reaction had taken place, that is, the addition of hydrogen iodide to the double bond. However, if allowed to stand seven or eight days the iodides were reduced to the corresponding saturated derivative, symmetrical phenyl-p-chlorophenyl ethane.

The iodides formed from p-chlorostilbene were undoubtedly mixtures of phenyl-p-chlorobenzyl-methyl-iodide and p-chlorophenyl-benzyl-methyl-iodide. In order to determine the ratio in which the two iodides were formed, a melting point curve was constructed from the melting points of known mixtures of pure phenyl-p-chlorobenzyl-methyl-iodide and p-chlorophenyl-benzyl-methyl-iodide obtained from the corresponding alcohols. With the aid of this curve, the composition of various mixtures could be determined.

¹⁰The addition of hydrogen iodide to p-chlorostilbene was incomplete in glacial acetic acid solution, 50% of the reaction product being a brown gummy oil whose composition could not be determined.

The following fractions were isolated from the addition of hydrogen iodide to p-chlorostilbene in benzene solution.

From $C_6H_5CH^*CH=CHC_6H_4Cl$ ¹¹	g. $C_6H_5CHICH_2C_6H_4Cl$	g. $C_6H_5CH_2CHIC_6H_4Cl$
0.66 g., M.P. 69-72°	0.59	0.07
0.41 g., M.P. 58-62°	0.27	0.14
0.21 g., M.P. 52-56°	0.09	0.12
0.11 g., oil.		

Of the total solid product, 74.2% is phenyl-p-chlorobenzyl-methyl-iodide. Of the entire reaction product, including the oil, 68.3% is phenyl-p-chlorobenzyl-methyl-iodide.

From $C_6H_5CH=CHC^*H_4Cl$	g. $C_6H_5CHICH_2C_6H_4Cl$	g. $C_6H_5CH_2CHIC_6H_4Cl$
0.58 g., M.P. 70-71°	0.52	0.06
0.48 g., M.P. 58-65°	0.32	0.16
0.10 g., M.P. 54-55°	0.05	0.05
0.33 g., oil		

Of the total solid product, 76.7% is phenyl-p-chlorobenzyl-methyl-iodide. Of the entire reaction product, including the oil, 59.7% is phenyl-p-chlorobenzyl-methyl-iodide.

The first addition of hydrogen iodide to p-chlorostilbene in n-heptane was allowed to proceed for seven days and only symmetrical phenyl-p-chlorophenyl-ethane was obtained. When allowed to run only two days a mixture of the iodides was isolated from the oily reaction product. In this case, too, the mixture contained a larger proportion (about 80%) of phenyl-p-chlorobenzyl-methyl-iodide.

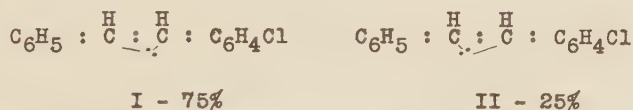
The results of the reactions in heptane indicated that hydrogen iodide first formed the iodide addition products and

¹¹The asterisk is used in these and subsequent formulae for p-chlorostilbene to indicate the carbon atom to which the hydroxyl group was attached in the original alcohol.

that these compounds were then reduced by the excess hydrogen iodide to the corresponding ethane derivative. This supposition was confirmed when it was found that, upon allowing the reaction in benzene (which gave the normal addition in two days) to proceed for seven days, the iodides formed were reduced to symmetrical phenyl-p-chlorophenyl-ethane.

In no case did the addition product with hydrogen iodide indicate the presence of a pure electromer of p-chlorostilbene. It is very possible that the unsaturated compound existed in electromeric form when first prepared from the carbinol but, owing to the instability of one form, it immediately changed into an equilibrium mixture of the two.

Approximately 75% of the solid iodides isolated was phenyl-p-chlorobenzyl-methyl-iodide, indicating an initial electromeric equilibrium of the following order:



According to the table of electronegativity,² the phenyl radical is more electronegative than the p-chlorophenyl radical and would tend to repel the doublet toward the carbon atom adjacent to the p-chlorophenyl radical, making electromer I the more stable form of p-chlorostilbene. This accounts for the formation of a larger amount of phenyl-p-chlorobenzyl-methyl-iodide, the hydrogen iodide addition product of electromer I.

As previously indicated, it was desirable to compare the properties of trans-p-chlorostilbene with the cis isomer. For this purpose, p-chlorotolane was prepared from p-chlorostilbene-dibromide.

Paal and Stiedewitz¹² have reduced toluene to iso-stilbene by using palladium as a catalyst, and this work with toluene was repeated before attempting the reduction of p-chlorotoluene. The iso-stilbene obtained was transformed into stilbene by the action of sunlight and a trace of iodine.

The reduction of p-chlorotoluene and the isolation of cis-p-chlorostilbene was carried out in a similar manner. Cis-p-chlorostilbene is an oil and cannot be mistaken for trans-p-chlorostilbene into which it was converted by the action of sunlight in the presence of a trace of iodine. By further hydrogenation in the presence of palladium, cis-p-chlorostilbene was completely reduced to the saturated compound, symmetrical phenyl-p-chlorophenyl-ethane.

The reaction of cis-p-chlorostilbene with hydrogen iodide was observed after two days and also after seven days. In both cases, only the completely reduced compound, symmetrical phenyl-p-chlorophenyl-ethane was isolated. The reaction was then repeated and the solution examined after short time intervals had elapsed in order to determine if the iodide was formed at any time during the course of the reaction. The first reaction was a conversion of the cis-p-chlorostilbene to the solid trans form, and this was present in the solution for the first three hours of the reaction. After five hours, an iodide was obtained which was identified as a mixture of about 90% phenyl-p-chlorobenzyl-methyl-iodide and 10% p-chlorophenyl-benzyl-methyl-iodide. The residue was in the form of an oil whose composition could not be determined. The iodide remained as the reaction product for 36 hours. After 48 hours, symmetrical phenyl-p-chlorophenyl-ethane was again isolated.

¹²Paal and Stiedewitz, Ber., 63, 766 (1930).

From these results it seems very improbable that geometric isomers could be mistaken for electronic isomers, and it is difficult to believe that the two forms of 2-pentene are merely cis and trans modifications. In the presence of hydrogen bromide, the unstable cis-2-pentene would immediately be converted into the trans isomer and there would be no difference in the subsequent behavior of these substances.

In order to compare the rate of formation of the iodides from the cis and trans isomers, a similar reaction was carried out with p-chlorostilbene. In this case, the unsaturated compound persisted for seven hours. After this time, a mixture of iodide and p-chlorostilbene was isolated from the reaction solution. Complete addition had taken place after twelve hours, as compared with five hours required for formation of the iodide from the cis isomer.

EXPERIMENTAL

Intermediate Grignard addition product.--An ether solution of p-chlorobenzylmagnesium bromide was prepared from 20.55 g. (1.5 moles) of p-chlorobenzyl bromide and 4.2 g. (2.6 moles) of magnesium turnings in dry ether. After refluxing on a water bath for twenty minutes, the mixture was siphoned through a closed filter to remove the excess magnesium. To this solution, which was dark green in color,¹³ was added a solution of 7.07 g. (1 mole) of benzaldehyde (freshly distilled in vacuum) in 100 cc. of ether. When all the benzaldehyde had been added, the solution, which had gradually faded from green to a faint greenish yellow at the end of the reaction, was refluxed on a water bath for two hours. The precipitate formed on standing, or, in some cases, formed while the last of the benzaldehyde solution was being added, was separated by decanting off the supernatant ether solution and washing several times with dry ether. It was then dried in a vacuum desiccator over phosphorous pentoxide. The substance was quite stable in air and did not take up moisture rapidly. It reacted slowly with acids and bases with the liberation of heat.

Anal. Calcd. for $C_{18}H_{22}O_2MgBrCl$: Cl, 8.65; Br, 19.50. Found: Cl, 8.68, 8.74; Br, 19.55, 19.70.

¹³Bachman (J.A.C.S., 53, 2759 [1931]) has reported the formation of a colored solution during the course of the reaction between triphenylmethylmagnesium bromide and benzophenone. He attributes the color to the presence of two free radicals, bromomagnesium ketyl and triphenylmethyl. Inasmuch as the green color under consideration was formed in the preparation of the Grignard reagent and gradually disappeared during the addition of the aldehyde, it is possible that it is due either to a free radical formed from the Grignard reagent itself or to an oxidation product of the p-chlorobenzylmagnesium bromide.

The ether-free intermediate Grignard addition product was prepared by heating a weighed amount of the etherate in vacuo at 100° to remove the ether.

Anal. Calcd. for $C_{14}H_{12}OMgBrCl$: Cl, 10.56; Br, 23.80. Found: Cl, 10.71, 10.61; Br, 24.14, 23.91.

The etherate was formed by allowing the ether-free substance to stand in a desiccator, evacuated to 350 mm., with anhydrous ether.

Anal. Calcd. for $C_{18}H_{22}O_2MgBrCl$: $(C_2H_5)_2O$, 0.0329. Found: $(C_2H_5)_2O$, 0.0332.

Phenyl-p-chlorobenzyl-carbinol was prepared by hydrolyzing the intermediate Grignard addition product with ice and sulphuric acid and extracting the alcohol with ether. The ether solution was dried over anhydrous sodium sulphate, the ether was removed and the residue was crystallized from petroleum ether. Yield 52%. M.P. 60°.

Anal. Calcd. for $C_{14}H_{13}OCl$: Cl, 15.24. Found: Cl, 15.14.

p-Chlorostilbene.--Phenyl-p-chlorobenzyl-carbinol was dissolved in dry benzene and warmed on a hot plate with phosphorous pentoxide. The benzene solution was decanted and allowed to evaporate. The white residue, p-chlorostilbene, crystallized from petroleum ether melted at 130°.

The preparation of the intermediate Grignard addition product of p-chlorophenyl-benzyl-carbinol was carried out in the same manner as the Grignard reaction previously described, using 4.22 g. (2.6 moles) of magnesium turnings, 12.67 g. (1.5 moles) of benzyl chloride and 9.38 g. (1 mole) of p-chlorobenzaldehyde. The same color change was observed in this reaction although the green was not as intense as that of the solution of p-chlorobenzylmagnesium bromide. After refluxing the final mixture for

two hours, the solution was filtered into a dry flask and 100 cc. of sodium dried low boiling petroleum ether was slowly added through a dropping funnel with vigorous stirring. The precipitate, which began to form after about 75 cc. of petroleum ether had been added, changed, on further addition of the solvent, to a heavy yellow oil which settled to the bottom of the flask and was separated from the supernatant liquid. On stirring, the oil changed to a gummy mass which broke down into a fine, dry, slightly yellow powder.

Anal. Calcd. for $C_{18}H_{22}O_2MgCl_2$: Cl, 19.41. Found: Cl, 23.50, 23.02, 21.71, 22.61.

The ether-free intermediate Grignard addition product of p-chlorophenyl-benzyl-carbinol was prepared by heating a weighed amount of the addition product in vacuo at 100° to constant weight.

Anal. Calcd. for $C_{14}H_{12}OMgCl_2$: Cl, 24.34. Found: Cl, 24.46, 24.56.

An attempt was made to convert the ether-free compound into the etherate by allowing it to stand in a desiccator with anhydrous ether. The substance took up ether quite readily but when it was removed from the atmosphere of ether in the desiccator, it lost weight very rapidly. Analysis of the substance showed that only a small amount of the etherate had been formed.

Anal. Calcd. for $C_{18}H_{22}O_2MgCl_2$: Cl, 19.41. Found: Cl, 23.31, 22.95.

p-Chlorophenyl-benzyl-carbinol was extracted from the Grignard reaction mixture in the same manner as was phenyl-p-chlorobenzyl-carbinol. The product was in the form of a colorless oil which partially crystallized after standing seven days. The alcohol crystallized slowly from a hot petroleum ether solu-

tion. Yield, 48%. M.P. 56°.

Anal. Calcd. for $C_{14}H_{13}OCl$: Cl, 15.24. Found: Cl, 15.28.

p-Chlorostilbene prepared from p-chlorophenyl-benzyl-carbinol by treating its benzene solution with phosphorous pentoxide melted at 130°. Its melting point was not lowered by addition of the dehydration product of phenyl-p-chlorobenzyl-carbinol.

Phenyl-p-chlorobenzyl-methyl-iodide.--The hydrogen iodide used in the preparation of the iodides was prepared from potassium iodide and syrupy phosphoric acid (made by heating phosphoric acid until it was opaque and viscous) and purified by passing through a tube of moist red phosphorous and glass beads to remove iodine and through a tube of phosphorous pentoxide to remove moisture. A trap cooled in a freezing mixture, placed after the phosphorous pentoxide tube, removed phosphorous triiodide which was carried over with the gas. The hydrogen iodide was then passed into a flask containing the solvent and closed to the air by a calcium chloride tube.

Phenyl-p-chlorobenzyl-carbinol (1.1 g.) was added to a solution of 9 g. of hydrogen iodide in 50 g. of glacial acetic acid and the mixture allowed to stand in a glass stoppered bottle for 36 hours at room temperature. The acid solution was then poured on to ice and extracted with benzene. The benzene solution was washed free of acid with ice water and free of iodine with dilute sodium thiosulphate solution. After drying over sodium sulphate, the benzene was removed and the solid residue of the iodide was crystallized from petroleum ether. Yield, 67.7%. M.P. 82°.

Anal. Calcd. for $C_{14}H_{12}ICl$: I, 37.06. Found: I, 35.92.

p-Chlorophenyl-benzyl-methyl-iodide.--p-Chlorophenyl-

benzyl-carbinol (1.3 g.) and hydrogen iodide (8 g.) were allowed to react in glacial acetic acid solution for 42 hours at room temperature. The product was then extracted in the usual manner and crystallized from petroleum ether. Yield, 57.5%. M.P. 74.5°.

Anal. Calcd. for $C_{14}H_{12}ICl$: I, 37.06. Found: 35.10.

Addition of hydrogen iodide to p-chlorostilbene.--One gram each of the unsaturated compound derived from p-chlorophenyl-benzyl-carbinol and from phenyl-p-chlorobenzyl-carbinol was treated with an excess of hydrogen iodide using three solvents: glacial acetic acid, benzene and n-heptane.

In glacial acetic acid the unsaturated compounds were allowed to react with 9.5 g. of hydrogen iodide for 20 weeks in the refrigerator. The solidified mass was then melted and extracted with benzene, washed free of acid and iodine and dried. On removal of the benzene, a gummy residue remained from which only 25% of the theoretical amount of iodide could be isolated.

In benzene, 8.5 g. of hydrogen iodide were used for each gram of unsaturated compound. After standing 48 hours at room temperature the solution was washed free of acid and iodine and dried over sodium sulphate. On removal of the benzene, a solid residue remained which was crystallized from petroleum ether. Yield, from $C_6H_5\overset{*}{CH}=CHC_6H_4Cl$, 1.28 g.; from $C_6H_5CH=\overset{*}{CH}C_6H_4Cl$, 1.14 g. A discussion of the composition of the mixture formed on addition of hydrogen iodide to p-chlorostilbene was given in the theoretical part of this dissertation.

A solution of 8.5 g. of hydrogen iodide in 32 g. of n-heptane was divided equally between one gram each of the two unsaturated compounds. The solutions were kept in the refrigerator for nine hours, then at room temperature in the dark for six days. At the end of this time both solutions were dark brown with iodine

and each bottle contained solid iodine. The mixtures were washed free of acid and iodine and dried over sodium sulphate. From both substances there was a 97.5% yield of an iodine-free solid, which proved to be symmetrical phenyl-p-chlorophenyl-ethane. Crystallized from petroleum ether, it melted at 45-45.5°.

Anal. Calcd. for $C_{14}H_{13}Cl$: C, 77.61; H, 6.01; Cl, 16.38.
Found: C, 77.32; H, 6.09; Cl, 16.13, 16.24.

The preparation of p-chlorostilbene-dibromide.--p-Chlorostilbene was dissolved in carbon disulfide and a solution of bromine in carbon disulfide was added until the solution was no longer decolorized when exposed to the rays of an 100 watt Mazda lamp. On evaporation of the solvent, a white solid remained which was crystallized from benzene. M.P. 202°.

Anal. Calcd. for $C_{14}H_{11}Br_2Cl$: Br, (1 atom) 21.35. Found: Br, 21.90.

The preparation of p-chlorotolane.--By refluxing a mixture of p-chlorostilbene-dibromide with alcoholic potassium hydroxide for fifteen hours, two moles of hydrogen bromide were removed. Water was added to the reaction solution and, after acidifying, the precipitate of p-chlorotolane was analyzed for chlorine while the filtrate was analyzed for bromide ion.

Anal. filtrate. Calcd. for $C_{14}H_{11}Br_2Cl$: Br, (2 atoms), 42.70.
Found: Br, 42.61.

Anal. precipitate. Calcd. for $C_{14}H_9Cl$: Cl, 16.69. Found: Cl, 16.10, 16.19.

Reduction of tolane.--The apparatus used for the reduction process was essentially the same as that employed by Paal¹² except that it was made with a glass stoppered opening in the top through which the solvent, catalyst and substance to be reduced could easily be introduced. The reaction chamber was enclosed in

black paper. One of the outlets was connected to a gas burette, the other to the hydrogen supply. The hydrogen was purified by passing successively through alkaline potassium permanganate, concentrated sulphuric acid and silica gel. Thirty cc. of absolute methyl alcohol and a few fibres of palladium asbestos were placed in the reaction chamber and shaken with hydrogen until no more gas was absorbed. The tolane was then quickly added, and the reduction carried out until the theoretical amount of hydrogen for half reduction had been taken up. The solution was filtered from the catalyst and the methyl alcohol removed in a vacuum desiccator, protected from light. The residue was an oil which, when dissolved in carbon disulfide and treated with a small crystal of iodine in the presence of bright sunlight, was transformed into a solid melting at 119° . This was identified as stilbene by a melting point of a mixture with pure stilbene.

The reduction and isolation of p-chlorotolane were carried out in the same way as that of tolane. The oily product was identified as cis-p-chlorostilbene by conversion into the trans isomer by means of a trace of iodine in the presence of strong sunlight. The solid obtained melted at 124° ; a mixture of this and pure trans-p-chlorostilbene (M.P. 130°) melted from 125 to 127° .

Cis-p-chlorostilbene was reduced to symmetrical phenyl-p-chlorophenyl-ethane (M.P. 45°) by shaking the methyl alcohol solution in the presence of palladium asbestos until no more hydrogen was taken up.

Reduction of trans-p-chlorostilbene.--Using palladium asbestos, p-chlorostilbene was quantitatively converted to symmetrical phenyl-p-chlorophenyl-ethane, M.P. 45° .

Addition of hydrogen iodide to cis-p-chlorostilbene.--A solution of 3.65 g. of hydrogen iodide in 29.5 g. of benzene and 0.09 g. of cis-p-chlorostilbene was allowed to stand seven days. At the end of this time, symmetrical phenyl-p-chlorophenyl-ethane was isolated from the reaction mixture. The addition was repeated removing samples at short time intervals. The first sample, removed after one hour, consisted of trans-p-chlorostilbene, and this was still present in the solution after three hours. After five hours, the solution yielded an oil from which a few crystals were separated melting at 70-80°. This product proved to be phenyl-p-chlorobenzyl-methyl-iodide. After 36 hours, the residue was still an oil containing iodine. After 48 hours, the residue was oily but contained no iodine. A few crystals were formed on cooling. These melted at 45° and were found to be symmetrical phenyl-p-chlorophenyl-ethane.

Additional reactions of hydrogen iodide on p-chlorostilbene.--The addition of hydrogen iodide to p-chlorostilbene in benzene was followed hour by hour. After seven hours, the reaction mixture still consisted largely of the unsaturated compound. After standing twelve hours, there was complete addition of hydrogen iodide. At the end of seven days the iodide was reduced to symmetrical phenyl-p-chlorophenyl-ethane.

The reaction of hydrogen iodide on p-chlorostilbene in n-heptane, which formed symmetrical phenyl-p-chlorophenyl-ethane after six days, was repeated and the reaction stopped after two days. An iodide melting at 63-72° was isolated from the oily residue, and proved to be composed to the extent of about 80% of phenyl-p-chlorobenzyl-methyl-iodide.

SUMMARY

1. The following new compounds have been prepared and analyzed: phenyl-p-chlorobenzyl-carbinol, the intermediate Grignard addition product (in both etherate and ether-free form) in the preparation of phenyl-p-chlorobenzyl-carbinol, p-chlorophenyl-benzyl-carbinol, the intermediate Grignard addition product (in both etherate and ether-free form) in the preparation of p-chlorophenyl-benzyl-carbinol, phenyl-p-chlorobenzyl-methyl-iodide, p-chlorophenyl-benzyl-methyl-iodide, p-chlorostilbene-dibromide, p-chlorotolane and symmetrical phenyl p-chlorophenyl-ethane.

2. The addition of hydrogen iodide to p-chlorostilbene prepared from phenyl-p-chlorobenzyl-carbinol and p-chlorophenyl-benzyl-carbinol has been studied.

3. The addition of hydrogen iodide to the trans and cis forms of p-chlorostilbene is described.

4. The reduction of various ethylene and acetylene bonds is described.

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